Summary

These days, synthetic polymer-polymer complexes receive a lot of attention, not only from a scientific point of view, because of the analogy with complexes between biopolymers, playing a crucial role in all kinds of biological systems, but also because of the wide range of practical applications such as membranes, column packings, hydrogels, controlled release systems, template polymerization, supports for catalysts, coatings, compatibilizers, new materials, etc. Because of the strongly cooperative nature of the interactions involved, kinetic factors are very important in the overall process of complexation, determining the morphologies of the materials formed, and consequently also influencing their properties.
For the first time, in this thesis a systematic study is presented on the overall process of complexation in a complexing system, taking into account all important variables. The system under consideration is the so-called "stereocomplex" that is formed by mixing it- and st-PMMA, employing suitable conditions. In Chapter 1, a short review is given on the phenomenon of polymer-polymer complexation and in particular on the complexation between it- and st-PMMA. In addition, in appendix 2 a discussion is given on the special topic of the apparent stoichiometries of complexation shown by the stereocomplex at certain conditions.

The main subject of this thesis, the overall proces of stereocomplexation, is discussed in chapters 2-7. In chapters 2-4 and 7 a general mechanistic model is developed, in terms of which, in principle, all results reported on the formation of stereocomplex, can be interpreted. Chapters 5 and 6 are dealing with the thermodynamic aspects of complexation.

Chapter 2 represents a study of the complexation process in dilute solution by means of viscometry and light scattering, as a function of temperature, time, and concentration, resulting in a merely phenomenological description of the complexation process. It appeared that the "complexing ability" of the solvent is strongly dependent on temperature. In a strongly complexing solvent the process consists of three stages: complexation, association of complexed chain sections, resulting in the formation of compact nanoparticles, and finaly aggregation of particles containing associates.

The complexation in bulk was studied by means of DSC and WAXS as a function of annealing time and temperature; the results are given in chapter 3. The material obtained was always partly crystalline. For low annealing temperatures, the samples showed multiple endotherms with different characteristics. A mechanistic model, in which subsequent crystallization of the complexed chain sections plays an important role, is presented which accounts for the observed phenomena. The critical sequence length necessary for complexation, and the mobility of the chains, and consequently the annealing temperature and molar mass of the polymers employed, are the most important parameters in the mechanistic model presented. At low annealing temperatures complexation proceeds much faster than subsequent crystallization resulting in a fringed-micellar kind of growth, while at higher annealing temperatures lamellar crystallization occurs directly. In addition, a mechanism is proposed for the formation of the double-stranded helical basic structure of the complex, giving an explanation for the fact that the formation of it is almost independent of chain length. In this mechanism, a right-handed and a left-handed double-stranded helix are formed next to each other, starting from a kink of st-PMMA, which subsequently wraps around the it-chain, followed by a rotation.
The endotherms are interpreted respectively as the decomplexation of complexed sections, partly organised into fringed-micellar clusters of complexes (T_m^1), and the simultaneous decomplexation and melting of lamellarly crystallized complexes (T_m^3). It was argued that the additional heat of crystallization of complexed sections is negligible, compared to the heat of complexation. Apart from these main endotherms also a small endotherm was found (T_m^2), which was assigned to the decomplexation of complexed sections, formed during scanning.

In chapter 4, the results are given of an investigation of the complexation in dilute solution by means of DSC applied to isolated complexed material, solution viscometry, and isothermal mixing calorimetry. Essentially the same mechanism as proposed for the complexation process in bulk can account for the observed phenomena, including the association and aggregation stages following complexation, reported in chapter 2. The main parameters in the proposed mechanism, the critical sequence length and the mobility of the chain sections, are influenced by various variables as solvent quality, temperature, mixing ratio, and tacticity.

Chapters 5-7 deal with the complexation between long "matrices" and much shorter "oligomers". Apart from the interest in

these systems, arising from the phenomenon of template polymerization, these systems are also very suitable to study the cooperative character of the interactions involved in complexation processes in general.
A theory to describe the complexation of homodisperse as well as heterodisperse "oligomers" with much longer "matrices" is introduced in chapter 5. It is predicted that a very strong selectivity with respect to oligomer chain length will be found. A simple relation for the critical chain length is derived, and it was shown that this parameter is independent of complexation stoichiometry. The ratio at which a maximum heat of complexation is found is predicted not only to be dependent on the complexation stoichiometry, but also on oligomer chain length, polydispersity, concentration, and solvent.

The results of a calorimetric study on it-/st-PMMA matrix-oligomer systems as a function of it-/st-mixing ratio, concentration, chain length, and tacticity, are given in chapter 6. The overall heat of complexation in DMF at 30°C (including heats of (de)solvation), is estimated to be 7.0 kJ/basemole of complex. Apart from a selectivity with respect to chain length, also a strong selectivity with respect to the more perfect stereoregular sequences, for the case of st-oligomers of low tacticity, was found to occur. The theory, developed in chapter 5, was applied to the experimental data and it followed that for low degrees of occupancy of the matrix, the calculated data from the theory are in quantitative agreement with the experimental values. Deviations from the predicted values are observed for higher degrees of occupancy of the matrix, which was ascribed to the subsequent crystallization of complexed sections. It is concluded that the theory is very suitable to describe matrix-oligomer complexation reactions, as long as equilibrium is approached.

The process of complexation between long it-matrices and much shorter st-oligomers was also investigated by means of DSC applied to complexed material, isolated from dilute solution, as a function of it-/st- mixing ratio, time after mixing, and chain length of the oligomers. The results are presented in chapter 7. In line with expectations, based on the general mechanism, developed in chapters 3 and 4, two endotherms were found, originating from decomplexation of complexed sections, partly organised into fringed-micellar clusters (T_m^1), and the simultaneous decomplexation and melting of lamellarly crystallized complexes (T_m^3). A dependence of T_m^3 on oligomer chain length was observed, suggesting that the (maximum) lamellar thickness was limited by this parameter. For the heat of com-

plexation a value of 20 KJ/basemole complex was found, while further evidence was obtained that the additional heat of crystallization of complexed sections is negligible, compared to the heat of complexation.

Chapter 8 deals with the special case of complexation between complementary stereoregular PMMA's, one of which is covalently bound to silica particles.
Silica bound highly isotactic PMMA, was synthesized by "initiation" of silica-bound methacrylate groups with phenylmagnesium bromide, followed by graft polymerization of subsequently added methyl methacrylate. This newly developed method, which is expected to be also applicable for synthesizing other polymers terminally attached to a silica surface, is described in appendix 3.
It was shown to be possible to separate and isolate it- and st-PMMA from preformed complexed material, employing the silica bound it-PMMA. In order to investigate the selectivity of the complexation with respect to chain length, the complexation between it-PMMA and silica bound at-PMMA in THF was studied, as for this system equilibrium conditions could be obtained. It was shown that the complexation is indeed highly selective with respect to chain length. However, from the results it also followed that the presence of the silica surface and in particular the local segment density in the surface layer, had a considerable influence on the amount of complex formed, as well as on the selectivity. The results are most probably the first direct indications that interactions between polymers attached to a surface and polymers in free solution are for an important part determined by entropic limitations.

Apart from the overall process of stereocomplexation, also the basic structure of the complex itself was subject of investigation. The results are presented in appendix 1. It was shown that the X-ray fiber data obtained, including a meridional reflection on the ninth layerline, could be explained in terms of a 9/1 double-stranded helix, having an asymmetric unit consisting of 1 it- and 2 st-units. An apparent two-fold axis of symmetry could be ascribed to the existance of a specific kind of disorder. The fact, that also in case of samples of low tacticity complex is formed, can be explained easily from the proposed structure. The driving force for complexation is most probably a good spatial fit between the chains stabilizing each other's energetically most favourable conformation by Van der Waals forces.